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Acidification of Aquatic and Terrestrial Systems
Chemical Weathering

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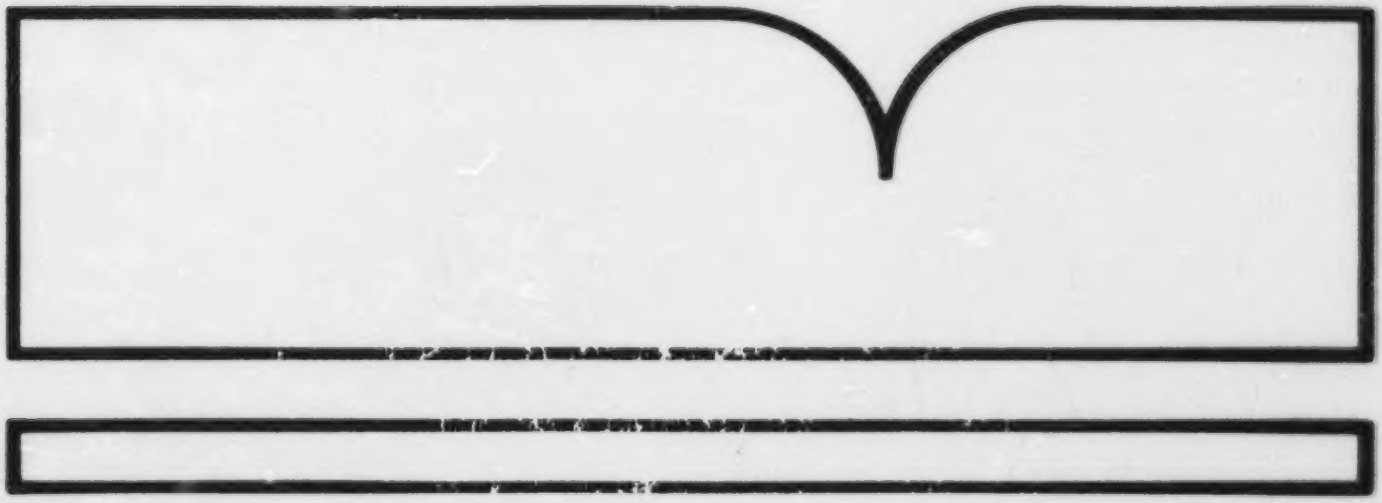

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Acidification of Aquatic and Terrestrial Systems: Chemical Weathering

by

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16. ABSTRACT

The pH and pε of the terrestrial and aquatic environment is determined by coupled reactions of oxidation-reduction and acid-base. If disturbances are created in elemental cycles of the environment (whereby oxidation of C, S, and N exceeds reduction reactions), a net production of H^+ ions is a necessary consequence. We have shown that aggrading biomass and humus and oxidation reactions (nitrification, sulfur oxidation) serve to add protons to aqueous systems, while chemical weathering, ion exchange, and reduction reactions (denitrification, H_2S production) serve to consume protons (add ANC to the water). Bar diagrams are a convenient means to examine changes in ANC or BNC in water and soils.

Atmospheric acid deposition creates an additional input of hydrogen and sulfate ions (H_2SO_4) to the terrestrial and aquatic ecosystem which is partly neutralized by increased weathering and cation export. It is balanced, in part, by aluminum dissolution and causes the negative effects in aquatic ecosystems on fish and possibly on forests.

The lakes which have been acidified by acid precipitation are those with extremely sensitive hydrologic settings and with watersheds lacking carbonate minerals. They tend to be small lakes. They respond relatively rapidly to changes in acid loading (on the order of a few hydraulic detention times). The soils of these watersheds have not been greatly acidified by acid precipitation nor has podzolization occurred due to anthropogenic acid deposition. However, this does not imply that more subtle changes in nutrient cycling or forest production could not have occurred. Soil solution pH could be reduced by the anthropogenic input of acids. We have proposed a quantitative framework with which to examine these questions.

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Abstract

Our global environment is on the average, with regard to a proton and electron balance, in a stationary state; schematically, the oxidation states and the H^+ reservoirs of the weathering sources equal those of the sedimentary products. Obviously, such balances are locally and regionally upset; in addition, they have become significantly disturbed by the combustion of fossil fuels which generates a net production of H^+ ions in atmospheric deposition.

In this chapter, we intend to show how this disturbance is transferred to the terrestrial and aquatic environment and to review the major H^+ yielding and H^+ consuming processes occurring in the watersheds, paying special attention (1) to the disturbance of the H^+ balance resulting from temporal or spatial decoupling of the production and mineralization of biomass, and (2) to the H^+ ion consumption by the weathering of rocks. The aggradation of vegetation (productive forests) may be accompanied by acidification of surrounding waters. In some instances, the acidic atmospheric deposition may be sufficient to disturb the existing H^+ balance between aggrading vegetation and weathering reactions.

Chemical weathering is shown to be a key process in neutralizing the internal production and the anthropogenic input of acids to a watershed. The lakes which have been acidified by acid precipitation are those lacking carbonate minerals and characterized by sensitive hydrological settings.

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1. INTRODUCTION

What controls the pH and the pε of our present-day environment*? Considering the schematic reaction,

$$\text{igneous rock} + \text{volatile substances} \rightleftharpoons \text{air} + \text{seawater} + \text{sediments} \qquad (1)$$

Sillen [1] gave the picture that volatiles (H_2O, CO_2, HCl, SO_2), the acids of volcanoes (i.e. the acids that have leaked from the interior of the earth), have reacted in a gigantic acid-base reaction with the bases of rocks (silicates, oxides and carbonates). Similarly, he calculated from the model system the quantities of redox components that have participated in a redox titration. On a global average, the environment is, with regard to a proton and electron balance, in a stationary situation which corresponds to a present-day atmosphere of 20.9% CO_2, 0.03% CO_2, 79.1% N_2 and a world ocean with pH = 8 and pε = 12.5.

This steady state is achieved by a global balance of oxidation and reduction and H^+ production and consumption. One can infer that above all, the rate of oxidation of reduced S, Fe, and C which occurs during the weathering of continental rocks is balanced by the rate of reduction of the

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*pε, a parameter for redox intensity, gives the (hypothetical) electron activity at equilibrium and measures the relative tendency of a solution to accept or transfer electrons. It is related to the equilibrium redox potential E_H (volts, hydrogen scale) by $p\varepsilon = -\log\{e^-\} = E_H/2.3\ RTF^{-1}$ (where R = gas constant, T = absolute temp, F = the Faraday; $RTF^{-1} = 0.059$ volts mol^{-1} at 25°C).

higher valent S, Fe and C into reduced forms during and after deposition in the sediments [2] Because transfer of electrons is coupled with the transfer of protons (to maintain charge balance), oxidation and reduction are accompained by proton release and proton consumption, respectively. Furthermore, the dissolution of rocks and the precipitation of minerals are accompained by H^+ consumption and H^+ production, respectively. Thus, the pε and pH of our present global environment reflect the levels where the oxidation state and the H^+ ion reservoirs (cf. alkalinity or acidity definitions given below) of the weathering sources equal those of the sedimentary products.

Obviously, in local environments, H^+ and e^- balances are upset and significant variations in pH and pε occur. The weathering cycle is also affected at least locally and regionally by our civilization. Redox conditions in the atmosphere are disturbed by enhanced rates of artifical weathering of fossil fuel. The combustion of these fuels leads to a disturbance in the e^--balance. The reactions of the oxidation of C, S and N exceed reduction reactions in these elemental cycles. A net production of H^+ ions in atmospheric precipitation is a necessary consequence [3]. The disturbance is transferred to the terrestrial and aquatic environment, where either oxidized species are reduced or acidity is neutralized via acid-base reactions. Oxidation reactions in the terrestrial and aquatic environemnt and assimilation processes by aggrading vegetation can produce local acidification in watersheds which may rival acid loading from the atmosphere.

It is the objective of this discussion to briefly review the major H^+ yielding and H^+ consuming processes occurring in watersheds; specifically, to elaborate the influence of chemical weathering, sediment formation, biological

assimilation (and humus formation) on the proton balance. An attempt will be made to give unifying definitions of acid or base neutralizing capacity (alkalinity and acidity, respectively) with respect to some reference level for the various subsystems of a watershed environment.

2. GENESIS OF ACID PRECIPITATION

Figure 1 illustrates the genesis of acid precipitation. Most of the major and minor gaseous components of the atmosphere (O_2, N_2, CO_2, CO, NO, NO_2, SO_2, CH_4) participate in elemental cycles which are governed by oxidation-reduction reactions mostly of biological origin; photosynthesis and respiration are major reactions in this cycle. The atmosphere is more susceptible to anthropogenic impacts than the terrestrial or the aqueous environment because, from a quantitative point of view, the atmosphere is much smaller than the other reservoirs. Furthermore the time constants concerning atmospheric alterations are small in comparison to those of the seas and the lithosphere. When the rate of oxidation of carbon, nitrogen, and sulfur increases relative to the rate of reduction of CO_2, nitrogen, oxides of nitrogen, SO_2 and H_2SO_4 (which is caused by the activities of civilization during the fossil fuel age), then the delicate balance is disturbed. Accordingly, the concentration of CO_2 has increased globally and the concentrations of SO_2, H_2SO_4, NO, NO_2, HNO_2 and HNO_3 have increased regionally. Buffering of these interactions in other reservoirs is slow. For example, the mixing time of the ocean is on the order of 1000 years. Since a modification of the redox balance corresponds to a modification of the acid-base balance the potential acidity of the atmosphere increases vis-a-vis the bases (Figure 1, upper part). Resulting from the oxidation of sulfur and nitrogen in the atmosphere, the strong acids H_2SO_4 and HNO_3 are the main participants in the formation of acid rain.

A considerable portion of the strong acids originate from the oxidation of sulfur in the combustion of fossil fuels and the "fixation" of nitrogen from the atmosphere to NO and NO_2 (during the combustion of gasoline in motor vehicles or other combustion processes of sufficently high temperature). HCl results from the combustion and decomposition of organochlorine compounds, for example, in polyvinyl chloride plastics during incineration. But it should also be mentioned that there exists natural sources resulting from volcanic activity and the oxidation of hydrogen sulfide from anaerobic sediments as well as dimethyl sulfide and other volatile organic sulfur compounds originating from the ocean. Bases originate in the atmosphere as the carbonates of wind-blown dust and from ammonia, generally of natural origin. The NH_3 originates from NH_4^+ ions and from the decomposition of urea found in soil environments. Redox and acid-base reactions occur in the gas phase, in aerosols, in rain drops, cloud droplets and fog.

The reactions of oxidation of SO_2 in the atmosphere yield a sulfur residence time of several days at the very most; this corresponds to a transport distance of hundreds to a thousand kilometers. The formation of HNO_3 by oxidation is more rapid, and compared to H_2SO_4, this results in a shorter travel distance from the emission source. H_2SO_4 can also react with NH_3 to form NH_4HSO_4 or $(NH_4)_2SO_4$ aerosols. In addition, NH_4NO_3 aerosols are in equilibrium with $NH_3(g)$ and $HNO_3(g)$. The importance of gas and aerosols scavenging by atmospheric condensates and rain drops depends on many factors.

Subsequent to the deposition, there are various processes in the terrestrial and aquatic environment that can neutralize or enhance the acidity of the precipitation. Of the processes depicted in Fig. 1, denitrification, sulfate reduction and chemical weathering decreases acidity, while photosynthetic assimilation and nitrification increase the acidity of the

waters (Table 1). For a better understanding of the factors that effect the H-balance, we first need to review some definitions.

3. ACID- OR BASE-NEUTRALIZING CAPACITY

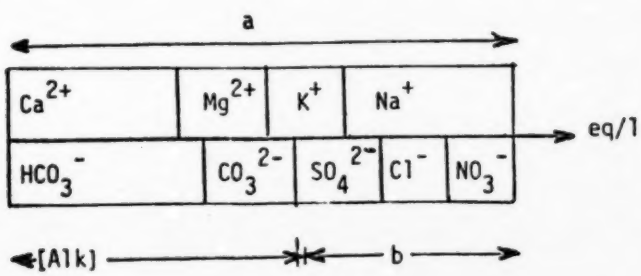
One needs to distinguish between the H^+ concentration (or activity) as an intensity factor and the availability of H^+, the H^+ ion reservoir, as given by the base-neutralizing capacity, BNC, or acidity [H-Acy]. The base neutralizing capacity [=HAcy] may be defined by a net proton balance with regard to a reference level, i.e., the sum of the concentrations of all the species containing protons in excess minus the concentrations of the species containing protons in deficiency of the proton reference level. For natural waters a convenient reference level (corresponding to an equivalence point in alkalimetric titrations) is H_2O, H_2CO_3:

$$[\text{H-Acy}] = [H^+] - [HCO_3^-] - 2[CO_3^{2-}] - [OH^-] \qquad (2)$$

The acid neutralizing capacity, ANC or alkalinity [Alk] is related to [H-Acy] by

$$-[\text{H-Acy}] = [\text{Alk}] = [HCO_3^-] + 2[CO_3^{2-}] + [OH^-] - [H^+] \qquad (3)$$

Considering a charge balance for a typical natural water



(4)

we realize that [Alk] (and [H-Acy]) can also be expressed by a charge balance, the equivalent sum of conservative cations minus the sum of conservative anions* ([Alk] = a - b):

$$\begin{aligned}[Alk] &= [HCO_3^-] + 2[CO_3^{2-}] + [OH^-] - [H^+] \\ &= [Na^+] + [K^+] + 2[Ca^{2+}] + 2[Mg^{2+}] - [Cl^-] \\ &\quad - 2[SO_4^{2-}] - [NO_3^-] \end{aligned} \tag{5}$$

The [H-Acy] for this particular water, obviously negative, is defined ([H-Acy] = b - a) as

$$\begin{aligned}H\text{-}Acy &= [Cl^-] + 2[SO_4^{2-}] + [NO_3^-] - [Na^+] \\ &\quad - [K^+] - 2[Ca^{2+}] - 2[Mg^{2+}] \end{aligned} \tag{6}$$

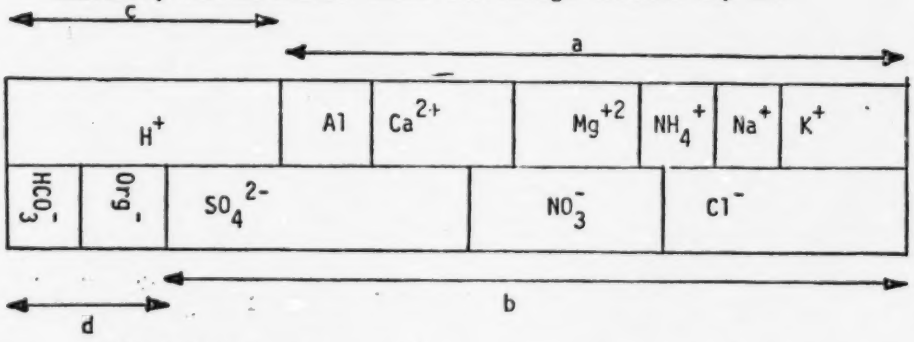
The definitions given for proton balance and electroneutrality agree rigorously because the reference state has been defined in terms of uncharged species. If the water under consideration contains other acid or base consuming species one needs to extend the proton reference level to the other components. If a natural water contains, in addition to the species given, organic molecules such as humic or fulvic acids (which may be represented by the summarizing formula HOrg) and ammonium ions, we can extend the reference level to include these species in the form of neutral molecules HOrg, NH_3; [Alk] would now be defined as:

---

*The conservative cations are the so-called base cations (historically, the cations of the strong bases-$Ca(OH_2)$, KOH, etc.) and the conservative anions are those anions which are the conjugate bases of strong acids (SO_4^{2-}, NO_3^-, Cl^-, etc.).

$$[Alk] = [HCO_3^-] + 2[CO_3^{2-}] + [Org^-] + \underbrace{[OH^-]}_{\text{negligible}} - [H^+]$$
$$= 2[Ca^{2+}] + 2[Mg^{2+}] + [NH_4^+] + [K^+] + [Na^+] - [2\,SO_4^{2-}] - [NO_3^-] - [Cl^-] \quad (7)$$
$$= -[H\text{-}Acy]$$

Similarly for an acidic water the charge balance may be:



(8)

$$[H\text{-}Acy] = b - a = c - d$$
$$= [H^+] - [HCO_3^-] - 2[CO_3^-] - [Org^-] \quad (9)$$
$$= 2[SO_4^{2-}] + [NO_3^-] + [Cl^-] - 3[Al^{3+}] - 2[Ca^{2+}] - 2[Mg^{2+}] - [NH_4^+] - [Na^+] - [K^+]$$

If NH_3 is chosen as a zero-level reference state, $[NH_4^+]$ is counted (as we have done here) as a cation of a strong base to belong to the excess positive charge from strong bases. Alternatively one could have chosen NH_4^+ as a reference state in the proton balance (because at the CO_2-equivalance point, NH_4^+ is the principle component). Then the rigorous identity between charge balance and H^+ balance no longer exists. Since we are here primarily concerned with change in alkalinity or acidity, it is preferable to choose as a zero proton reference state the uncharged species, i.e., H_2O, CO_2, HOrg, H_3BO_3, NH_3, etc.

The overall change in alkalinity or H-Acy of a water can then readily be calculated from the stoichiometry of weathering reactions, ion exchange, redox processes and biological production and respiration. A simple accounting can be made: every base-cationic charge unit (Ca^{2+}, K^+, NH_4^+ etc.) that is removed from the water by whatever process is equivalent to a proton added to the water, and every conservative anionic charge unit (from anions of strong acids) (NO_3^-, SO_4^{2-}, Cl^- etc.) removed from the water corresponds to a proton removed from the water; or generally:

$$\Sigma\Delta[\text{base-cations}] - \Sigma\Delta[\text{conservative anions}] = +\Delta[\text{Alk}] = -\Delta[\text{H-Acy}] \qquad (10)$$

As Table 1 illustrates, every reaction can be written by a balanced stoichiometric equation, and the change in [Alk] can be read either from Eq. (10) or the H^+ needed to balance the reaction. Note that the uptake (or release) of uncharged species such as O_2, CO_2 in photosynthesis and respiration, N_2, NH_3 in N_2-fixation, denitrification, H_2S, or CH_4 has no effect on changes in the alkalinity or H-Acidity (cf. Table 1).

The advantage of balancing conservative charge units is that the method can readily be extended to other systems: to sediments, soils, rocks, and biota to account for changes in acid- or base neutralizing capacity of these systems (Fig. 2).

4. PROCESSES AFFECTING ACID-NEUTRALIZING CAPACITY, ANC

4.1 ANC of Soil

In weathering reactions alkalinity is added from the soil-rock system to the water:

$$\Delta[Alk]_{water} = -\Delta[Alk]_{soil,\ rock} \qquad (11)$$

As Fig. 2 illustrates, the acid neutralizing capacity of a soil is given by the bases, carbonates, silicates, and oxides of the soil system. In a similar way as for an aquatic system, alkalinity and acidity can be defined. If the composition of the soil is not known but its elemental analysis is given in oxide components, the following kind of accounting is equivalent to that given in Fig. 2

$$ANC = [Alk] = 6(Al_2O_3) + 2(CaO) + 2(MgO) + 2(K_2O) + 2(Na_2O) + 4(MnO_2) + 2(FeO) + ("NH_4OH") - 2(SO_3) - (HCl) - 2(N_2O_5) \qquad (12)$$

Sulfates, nitrates and chlorides incorporated or adsorbed are subtracted from ANC. On the basis of acid-balance alone, one cannot distinguish whether uptake by the soil of H^+ and the release of cations is caused by weathering or by ion exchange. Similarily the loss of SO_4^{2-} from the water accompanied by OH^- or [Alk] release may be caused by sulfate reduction (See Table 1) or by ion exchange.

4.2 Chemical Weathering

Figure 3 shows the processes which affect the acid neutralizing capacity of soils. Ion exchange occurs at the surface of clays and organic humus in various soil horizons. The net effect of ion exchange processes is identical to chemical weathering, i.e., hydrogen ions are consumed and basic cations(Ca^{+2}, Mg^{+2}, Na^+, K^+) (and alkalinity) are released. However the kinetics of ion exchange are rapid relative to those of chemical weathering (on the order of minutes compared to hours or even days). In addition, the pool of

Table 1: Processes which modify the H^+-Balance in Waters [3]

* Alk = alkalinity = acid neutralizing capacity
H-Acy = Mineral acidity.

	Changes in Alkalinity $\Delta[Alk] = -\Delta[H\text{-}Acy]$ Equivalents per mole reacted (reactant is underlined)*
1a) Weathering Reactions	
$\underline{CaCO_3\,(s)} + H^+ \rightleftharpoons Ca^{2+} + HCO_3^-$	+2
$\underline{Ca\,Al_2\,Si_2\,O_8\,(s)} + 2H^+ \rightleftharpoons Ca^{2+} + H_2O + Al_2\,Si_2\,O_5\,(OH)_4\,(s)$	+2
$\underline{K\,AlSi_3\,O_8\,(s)} + H^+ + 4\,1/2\,H_2O \rightleftharpoons K^+ + 2H_4SiO_4 + 1/2\,Al_2\,Si_2\,O_5\,(OH)_4\,(s)$	+1
$\underline{Al_2O_3 \cdot 3H_2O} + 6H^+ \rightleftharpoons 2Al^{3+} + 6H_2O$	+6
1b) Ion Exchange	
$2\,ROH + \underline{SO_4^{2-}} \rightleftharpoons R_2\,SO_4 + 2OH^-$	+2
$NaR + \underline{H^+} \rightleftharpoons HR + Na^+$	+1
2) Redox Processes (Microbial Mediation)	
Nitrification $\underline{NH_4^+} + 2O_2 \rightleftharpoons NO_3^- + H_2O + 2H^+$	−2
Denitrification $5CH_2O + 4\underline{NO_3^-} + 4H^+ \rightarrow 5CO_2 + 2N_2 + 7H_2O$	+1
Oxidation of H_2S $\underline{H_2S} + 2O_2 \rightarrow SO_4^{2-} + 2H^+$	−2
SO_4^{2-} - Reduction $\underline{SO_4^{2-}} + 2CH_2O + 2H^+ \rightarrow 2CO_2 + H_2S + H_2O$	+2
Pyrite Oxidation $\underline{FeS_2}\,(s) + 3\,3/4\,O_2 + 3\,1/2\,H_2O \rightarrow Fe(OH)_3 + 2SO_4^{2-} + 4H^+$	−4
3) Synthesis (→) and Decomposition (←) of Biomass and of Humus	
Photosynthesis with NO_3-Assimilation (→), Aerobic Respiration (←)	
$a\,CO_2\,(g) + b\,NO_3^- + c\,HPO_4^{2-} + d\,SO_4^{2-} + \ldots + g\,Ca^{2+} + h\,Mg^{2+} + i\,K^+ + f\,Na^+ + x\,H_2O$	+b+2c+2d
$+(b+2c+2d-2g-2h-i-f)\,H^+ \rightleftharpoons \{C_a\,N_b\,P_c\,S_d \ldots Ca_g\,Mg_h\,K_i\,Na_f\,H_{2O_m}\}_{Biomass}$	−(2g+2h+i+f)
$+(a+2b)\,O_2\,(g)$	
NH_4- Assimilation (→); Anaerobic Mineralization (back reaction)	
$a\,CO_2\,(g) + b\,NH_4^+ + \ldots \rightleftharpoons \{C_a \ldots N_b \ldots\}_{Biomass} + a\,O_2\,(g)$	−b
N_2-Fixation (half- reaction)	
$\ldots + \frac{b}{2}\,N_2\,(g) + \ldots \rightarrow \{\quad N_b \quad\}_{Biomass}$	0

*) In the build-up of biomass (or the exchange of ions) the uptake of each equivalent of anions causes an equivalent increase in alkalinity, and each equivalent of cations which is taken up results in an equivalent decrease of alkalinity. One comes to the same conclusion as long as the biomass or humus is formed of neutral components $\{(CH_2O)_a(NH_3)_b(H_3PO_4)_c(H_2SO_4)_d \ldots (Ca(OH)_2)_g (Mg(OH)_2)_h(KOH)_i(NaOH)_f(H_2O)_m\}$ and provided that one has written the corresponding stoichiometric equations for formation and decomposition.

exchangeable bases is small compared to the total ANC of the soil (Eq. 12). Thus there exists two pools of bases in soils; a small pool of exchangeable bases with relatively rapid kinetics and a large pool of mineral bases with the slow kinetics of chemical weathering. If chemical weathering did not replace exchangeable bases in acid soils of temperate regions receiving acidic deposition, the base exchange capacity would be completely diminished over a period of 50-200 years (see Table 2).

In the long run, chemical weathering is the rate limiting step in the supply of basic cations for export from watersheds. Surface waters usually are not at chemical equilibrium with regard to common minerals in soils or sediments with the possible exception of amorphous aluminum hydroxide [4]. The chemistry of natural waters is mostly kinetically controlled.

The genesis of podzolic acid soils stems from a chromatographic effect whereby bases are depleted from the upper soil profile and iron and aluminum are mobilized. Soil profiles become stratified into horizons, e.g. O,A,B, and C. In podzolic soils the organic "O" horizon is typically a 0-10 cm deep and contains the humus from leaf and litter decomposition. The A horizon is the uppermost "inorganic" soil horizon. In podzolic soils, it is depleted of basic cations and appears as a gray-to-white leached layer. The B horizon is classified as "spodic". It appears somewhat reddish and contains much of the iron and aluminum which were mobilized from above due to acidic conditions. As soil water percolates, it is somewhat neutralized by exchange reactions and chemical weathering, and the iron and aluminum precipitate or adsorb from solution.

Even in acid podzolic soils, there exist significant amounts of "fresh" minerals or weatherable bases available for dissolution. One reason is mechanical weathering, a physical process. Solifluction (the process of

Table 2. Time Required to Titrate Exchangeable Bases in a Podzolic Soil with Acid Precipitation (100 cm/yr) at pH 4

Horizon*	Depth (cm)	Sum of Bases# (meq/100gm)	Cation Exchange Capacity (meq/100gm)	% Base Saturation	Soil pH@	Time to Titrate Bases (yrs)
A2	0-5	1.8	9.7	19	4.4	12.0
B21H	5-13	0.9	16.7	5	4.9	9.7
B22I	13-33	0.6	8.0	7	5.3	16.0
B23I	33-43	0.4	6.4	6	5.4	5.4
B3	43-63	0.2	2.9	7	5.6	5.4
						Σ = 48.5 yrs.

* Soil is a brown podzolic soil (Haplorthod) from north central Wisconsin. Pence, sampled by U.S.D.A. S.C.S. on 5/8/80.

Bases were extracted with ammonium acetate.

@ Soil pH is 1:1 H_2O extract.

bedrock crack and surfacing on steep slopes) is an important mechanism in mountainous terrain. Freezing, thawing, and cracking of rocks also avails fresh minerals, a form of mechanical weathering. Especially in pit and mound topographies, tree-throw provides a significant amount of fresh minerals from the B and C soil horizons. Burrowing animals can do likewise. Finally, forest canopies provide a "base-pump" whereby basic cations taken from lower soil horizons are deposited in a more weatherable form on the surface of the soil during litter fall.

There are several factors which strongly affect the rate of chemical weathering in soil solution. These include:

- hydrogen ion activity of the solution
- ligand activities in solution
- dissolved CO_2 activity in solution
- temperature of the soil solution
- mineralogy of the soil
- flowrate through the soil
- grain size of the soil particles

For a given silicate mineral, the hydrogen ion activity contributes to the formation of surface activated complexes which determine the rate of mineral dissolution at pH<6. Also since chemical weathering is a surface reaction controlled phenomenon, organic and inorganic ligands (e.g. oxalate, formate, succinate, humic and fulvic acids, fluoride, and sulfate) may form other surface activated complexes which enhance dissolution [5-7]. (Some organics are known to form surface complexes which "block" dissolution.) Dissolved carbon dioxide is known to accelerate chemical weathering presumably due to its effects on soil pH and the aggresion of H_2CO_3. Increases in temperature generally increase the solubility of minerals and increases the

rate of chemical weathering [8]. Because mineral dissolution is kinetically controlled, increases in the rate of flow and decreases in the particle size can strongly increase the rate of chemical weathering [9].

Mineralogy is of prime importance. The Goldich [10] dissolution series, which is roughly the reverse of the Bowen crystallization series, indicates that chemical weathering rates should decrease as we go from carbonates → olivine → pyroxenes → Ca,Na - plagioclase → amphiboles → K-feldspars → biotite and muscovite → aluminum oxides. If the pH of the soil solution is low enough (pH < 4.5), aluminum oxides provide some measure of neutralization to the aqueous phase along with an input of monomeric inorganic aluminum. The key parameter which affects the activated complex and determines the rate of dissolution of the silicates is the Si/O ratio. The less is the ratio of Si/O, the greater is its chemical weathering rate. Anorthite and forsterite have Si/O of 1:4 while quartz has Si/O of 1:2, the slowest to dissolve in acid.

4.3 Aluminum Dissolution

When soils are quite acid, as in the Lange Bramke watershed of the Harz Mountains of West Germany near Gottingen, aluminum is not only liberated from the soil in the rooting zone, but it is at high concentrations on the fine roots (and mycorrhizal fungal associations) due to a sorptive equilibrium of Al^{+3} with negatively charged root surfaces (Figure 4). The importance of aluminum uptake by trees in acid soils and sorbed-Al effects on active and passive transport of nutrients to the tree are the subject of much current debate [11-14]. Like chemical weathering, Al-sorption is a surface controlled phenomenon.

The regions where acid deposition has been reported to affect lakes (Adirondacks, N.Y., southern Norway and Sweden) also have acid soils. These soils developed due to the leaching of basic cations over recent geologic time. Acidity of the upper soils is natural and principally caused by three phenomena: 1) a relatively low ANC of the soil, 2) an aggrading canopy whereby synthesis of biomass exerts an acidifying influence (Figure 1), and 3) the production of organic acids due to humics formation and decomposition. The last two are internal processes as opposed to acidic deposition which adds an additional source of acid to the system. Its magnitude in the hydrogen ion budget of the soils must be assessed on a case-by-case basis. Acidic deposition at the Hubbard Brook watershed, Hovattn watershed in southern Norway, and the Gardsjon watershed in Sweden, have contributed a large percentage of the total acid flux to the soil environment (15), thus decreasing the pH of the soil below "natural" levels and liberating additional Al^{+3} via chemical weathering and ion exchange.

Feldspars and other aluminum silicate minerals provide the bulk of the chemical neutralization in most watersheds affected by acidic deposition. The kinetics of weathering is fractional order in hydrogen ion activity (Table 3). Fractional order kinetics necessitate that decreases in pH of the soil solution are partially compensated by increases in base cation weathering, but not totally. At pH < 4.5, aluminum is the principal cation which together with hydrogen ion, makes a charge balance against increases in sulfate from acid deposition. At pH > 4.5, it is the basic cations(Ca^{+2}, Mg^{+2}, Na^{+}, K^{+},) which increase as a result of acidic deposition. To the extent that the sulfate anion can be sorbed by the soil matrix (an alkalinity anion must be exchanged into solution), this process also serves to neutralize acidic deposition, much as compensatory chemical weathering. Except in the

Table 3. Reaction Order for the Rate Law for the Dissolution of Minerals.

Mineral	Formula	Solution	Rxn. Order	Ref.
Dolomite	$(Ca,Mg)CO_3$	HCl	$\{H^+\}^{0.5}$	(21)
Bronzite	$(Mg,Ca)SiO_3$	HCl	$\{H^+\}^{0.5}$	(22)
Enstatite	$MgSiO_3$	HCl	$\{H^+\}^{0.8}$	(20)
Diopside	$CaMgSi_2O_6$	HCl	$\{H^+\}^{0.7}$	(20)
K-feldspar	$KAlSi_3O_8$	Buffer	$\{H^+\}^{0.33}$	(14)
Iron Hydroxide	$Fe(OH)_3$-Gel	Various Acids	$\{H^+\}^{0.48}$	(23)
Aluminum Oxide	δ-Al_2O_3	HCl	$\{H^+\}^{0.4}$	(7)

southeast U.S., most soils receiving acidic deposition are in a rough equilibrium with regard to input sulfate anions (16,17).

4.4 Biomass-Synthesis

Assimilation by vegetation of an excess of cations can have acidifying influences in the watershed which may rival acid loading from the atmosphere. The synthesis of a terrestrial biomass, e.g. on the forest and forest floor, could be written with the following approximate stoichiometry:

$$\begin{aligned} &800\ CO_2 \\ &6\ NH_4^+ \\ &4\ Ca^{2+} \\ &1\ Mg^{2+} \\ &2\ K^+ \\ &1\ Al(OH)_2 \\ &1\ Fe^{2+} \\ &2\ NO_3^- \\ &1 H_2PO_4^- \\ &1\ SO_4^{2-} \end{aligned} \xrightarrow[+\text{Photosynthesis}]{H_2O} \underbrace{\begin{aligned} &(CH_2O)_{800} \\ &(NH_3)_8 \\ &(H_3PO_4)_1 \\ &(H_2SO_4)_1 \\ &(CaO)_4 \\ &(MgO)_1 \\ &(Al(OH)_3)_1 \\ &(FeO)_1 \\ &(H_2O)_m \end{aligned}}_{\text{Biomass}} + 16H^+ + 804\ O_2 \qquad (13)$$

From a point of view of acid neutralizing capacity, the biomass may also be represented in terms of corresponding cations, anions, and bases (Fig. 2). It is evident from this equation and from [15] that the aggrading production of terrestrial vegetation is accompanined by an acidification of the surrounding waters, correspondingly the ANC of the biomass increases. The ashes of trees are alkaline. Every temporal or spatial decoupling of the production and mineralization of biomass leads to a modification of the H^+-balance in the environment. This is the result of intensive agricultural and forestry practices and seasonal

fluctuations. The release of H^+ by intensive growing vegetation (especially by forests used for wood exploitation), leads to leaching of base cations from the soil.

The interaction between acidification by an aggrading forest and the leaching (weathering) of the soil is schematically depicted in Fig. 5. If the weathering rate equals or exceeds the rate of H^+ release by the biota such as would be the case in a calcaerous soil, the soil will maintain a buffer in case cations and residual alkalinity. On the other hand, in non-calcereous "acid" soils, the rate of H^+ release by the biomass may exceed the rate of H^+ consumption by weathering and cause a progressive acidification of the soil. In some instances, the acidic atmospheric deposition may be sufficient to disturb an existing H^+-balance between aggrading vegetation and weathering reactions. A quantitative example is provided by the carefully established acidity budget in the Hubbard Brook Ecoxystem, Fig. 6 [18], where, because of acid deposition, the H^+ ion sources nearly balance the H^+ ion sinks.

Humus and peat can likewise become very acid and deliver some humic or fulvic acids to the water. Note that the release of humic or fulvic material ($HOrg$, Org^-) to the water in itself is not the cause of resulting acidity, but rather the aggrading humus and net production of base neutralizing capacity (see Gorham et al., this volume).

4.5 Redox Processes

Table 1 lists some changes in the proton balance resulting from redox process. Alkalinity or acidity changes can be computed as before: any addition of NO_3^- or SO_4^{2-} to the water as in nitrification or sulfur oxidation increases acidity while NO_3^- reduction (denitrification) and SO_4^{2-} reduction causes an increase in alkalinity. As shown by Schindler (this volume), in

experimental lakes, the nitrate removal caused by denitrification is linearily related to an increase in alkalinity. Incipient decreases of pH resulting from the addition of sulfuric acid or nitric acid to a lake is reversed by subsequent denitrification or SO_4^{2-} reduction.

Sediments in a water-sediment system are usually highly reducing environments. Electrons, delivered to the sediments by the "reducing" settling biological debris, and H^+ are consumed; thus in the sediments (including pore water) alkalinity increases, rendering the overlying water more acidic [19,20].

5. LAKE RESPONSE

The reaction of free acidity with crystalline minerals (granite, gneiss and mica schists) is much slower than the dissolution of carbonates. Therefore acid lakes are more likely to be found in crystalline rock areas. This is also true in Switzerland where about 20 small acid lakes are found in the alpine southern part. There, nature makes some very interesting experiments on the weathering of these minerals. These lakes are acid because the residence time of acid precipitation in soils and the watershed is relatively short. The soils in question are very thin with exposed and weathered rocks and only little fine materials available. The water has little time to react with the minerals. Also, trees or thick vegetation is lacking at these altitudes. Some typical waters in the Maggia Valley are schematically shown in Fig. 7. It illustrates the successive reactions and neutralization of the source water as it flows; the concentrations of cations (Al^{3+}, Ca^{2+}, K^+ and Na^+) and silicic acid increases as the dissolution process occurs.

In a first approximation, acidity is highest in those lakes with very small surface and catchment areas and the shortest residence time in the watershed. If the lakes receive runoff and snowmelt water very rapidly, then the acidity of its water is not greatly different from that of the snow.

The concentration of free aluminum can only increase to the solubility of aluminum oxide; the lower the pH, the higher is the soluble Al(III) concentration. Fish cannot reproduce in acid lakes; this is probably due to the high concentrations soluble Al(III) rather than to the concentrations of free acids. For the most part, the lakes are not sterile, but the supply of nutrients is extremly small. The water contains less than 5 µg P per liter, and thus the productivity is small too. It is interesting to note that the residual concentration of some heavy metal ions in the acid mountain lakes, far away from streets and civilization, is much higher than in "more polluted" lakes in the lowland (Sigg, this volume). Tne removal of these metals in the acid lakes is less efficient because of the lower sedimentation rates and because the lower pH of these waters reduces the tendency of heavy metals to become bound to the settling particles.

The rate of chemical weathering in the watersheds of these lakes can be calculated on the basis of the difference between precipitation acidity and that remaining in the lake; it amounts to 500 eq ha^{-1} yr^{-1} and is only about half of the rate of chemical weathering of alumino-silicate minerals in the apline valley of the Rhine.

5.1 Trickle-Down Model

A description of the time-variable version of the Trickle-down model has been presented in Schnoor *et al.* [22] and the steady state version has been given in Stumm *et al.* [3]. The model is based on a mass balance for alkalinity in the watershed and lake.

An input/output analysis for a lake can be expressed mathematically as:

$$V \frac{d(Alk)}{dt} = -IL_{acy} (1-f) - Q(Alk) + \frac{PV}{H} \quad (14)$$

where

V = water volume of the lake, L^3

Alk = alkalinity concentrations, eq/L^3

t = time, T

I = precipitation (inflow) volume per time, L^3/T

L_{acy} = total acidity of precipitation (dry + wet), eq/L^3

Q = outflow or seepage rate, L^3/T

f = fraction of acid neutralized in the watershed

P = alkalinity production by sediment, eq/L^2-T

H = mean depth of lake, L

Under steady state conditions and if the alkalinity contribution from sediments is negligible, the concentration in the lake is:

$$(Alk) = \frac{I}{Q} L_{acy} (f-1) \quad (15)$$

The fraction of acidic deposition that is neutralized in the watershed can be defined in terms of a watershed weathering rate, W.

$$f = W/[RL_{acy} (0.1)] \quad (16)$$

where

W = weathering rate, eq/ha-yr

R = precipitation rate, cm/yr

L_{acy} = total acidity input, μeq/L

The total acid input concentration, L_{acy}, must include any additional acid sources in the watershed which are significant relative to acidic deposition from the atmosphere. The rate of chemical weathering and leaching of soils is determined by the acidity of the soil water and the presence of organic and inorganic ligands. In sensitive watersheds, where water has little time to come into contact with soil minerals, the weathering of primary minerals in exposed rocks and sediments is sufficient to provide some neutralization.

Stumm et al. [6] have shown that the rate of weathering of δ-Al_2O_3 is proportional to the degree of surface protonation and to the surface complexation of oxalate in laboratory experiments.

$$R = k_1 \{\equiv\text{-}OH_2^+\}^3 + k_2\{\equiv\text{-}Ox\} \qquad (17)$$

where R = the rate of dissolution of aluminum oxide. Equation (17) results in a dissolution rate that is proportional to $\{H^+\}$ to the 0.4 power. Table 3 shows that many common minerals have been reported to undergo fractional order dissolution in acids.

An expression for chemical weathering (that is analogous to equation 17) is:

$$W = k_h \{H^+\}^m + k_o \qquad (18)$$

where

W = chemical weathering rate

k_h = rate constant for acid hydrolysis

m = fractional order constant

k_o = rate constant in the absence of free acidity (due to CO_2 and ligand weathering)

The fraction of acid neutralized in the watershed is related to the chemical weathering rate when the precipitation acidity penetrates the soil. From equation (16):

$$f = \frac{k_h L_{acy}^{m} + k_o}{RL_{acy}(0.1)} \tag{19}$$

By substituting equation (19) into equation (15), one obtains the following expression for steady state alkalinity as a function of total precipitation acidity:

$$(Alk) = \frac{A_d(k_h L_{acy}^{m} + k_o)}{Q} - \frac{I}{Q} L_{acy} \tag{20}$$

where

A_d = drainage area of the watershed, L^2

5.2 Evaluation of Coefficients

Equation (20) can be used to predict the alkalinity of lakes based on their total acidty input concentration (L_{acy}). It gives the steady state reaction progress for a lake at various acid loadings. The coefficient k_o can be determined from water chemistry survey data for lakes of sensitive mineralogy and hydrology that receive very low acid loadings. It is approximately 200 eq/ha-yr for lakes in most sensitive settings. The coefficients m and k_h can be determined based on two criteria: (1) field data to calibrate the model at a known acid loading and lake alkalinity; and (2) the mineralogy of the watershed compared to the reaction order for dissolution

in laboratory studies (Table 3). Table 4 gives a number of sensitive watersheds which receive varying amounts of acid deposition. The range of chemical weathering rates (200-1600 eq/ha-yr) is typical, and in general, the rates increase with increasing acid deposition. These watersheds were chosen as among the most sensitive in their region.

A reaction pathway for a lake beginning at point p (with 10 μeq/l alkalinity) is given in Figure 8 using the steady state model. Equation (20) was used for the calculation of the reaction pathway with k_o = 200 eq/ha-yr, m = 0.4, and k_h = 40 eq/ha-yr.

5.3 Time to Steady State

Equation (20) is actually a pseudo-steady state relationship, since it assumes that the soil neutralizing capacity is in excess. The time to achieve such a pseudo-steady state is relatively short (on the order of three hydraulic detention times of the lake). However, the pseudo-steady state alkalinity can decrease over a long time as minerals in the soil are titrated.

For situations where the watershed has extremely thin soils and very large acid deposition rates, the mineral phase may become exhausted. It can no longer supply basic cations to replenish the base exchange capacity of the soil, nor can it neutralize incident acid deposition. In this case, one must make a mass balance on the total acid neutralizing capacity (ANC) of both the water and the soil during their progressive titration.

The total ANC of the soil decreases over time:

$$\frac{dr}{dt} = -kr = \frac{-W}{Md} \qquad (21)$$

where

Table 4. Watershed Measurements and Calculated Weathering Rates for Sites Reported in the Literature

Lake	Alk, μeq/ℓ	R, cm/yr	Q/I	Lacy, μeq/ℓ	$\frac{I}{Q}$Lacy, μeq/ℓ	f	W, eq/ha-yr
N.C. Wisconsin	0	76	0.45	25	56	1.0	190
N.E. Minnesota	+54	71	0.30	14	47	2.1	230
Star., SWITZ.	-25	150	0.77	39	50	0.50	290
Langtjern, NOR.	-20	88	0.66	52	80	0.75	340
Birkenes*, NOR.	-33	140	0.77	57	74	0.55	440
Storgama, NOR.	-30	125	0.76	60	79	0.63	470
Gardsjon, SWEDEN	-25	113	0.59	63	107	0.77	550
Lange Bramke*, BRD	-32	104.5	0.6	100	167	0.81	840
Woods, N.Y.	-16	130	0.62	79	130	0.90	900
Hubbard Br.*, N.H.	-6.3	130	0.62	74	120	0.95	910
Solling*, BRD	-10 to -30	104.5	0.6	163	272	0.93	1,600

*denotes stream as opposed to lake setting

k = rate constant for soil neutralization, 1/T

d = effective depth of soil, L

M = bulk density of the soil, M/L^3

W = weathering (neutralization) rate, eq/L^2-T

r = total ANC of the soil, eq/M

Rewriting equation (14) as two equations:

$$\text{Lake Alkalinity} \quad \frac{d(Alk)}{dt} + \frac{Q}{V}(Alk) = -\frac{I}{V} L_{acy} + k \frac{V_{soil}}{V} Mr \tag{22}$$

$$\text{Soil ANC} \quad \frac{dr}{dt} = -kr \tag{23}$$

where

$$k = k' \left(\frac{[H^+]}{[H^+]_{ref}}\right)^m \left(\frac{\delta}{\delta_{ref}}\right)^s \left(\frac{Q_{soil}}{Q_{ref}}\right)^q \tag{24}$$

k' = reference rate constant, 1/T

δ = effective surface area of soils (particle size-related), L^2

Q_{soil} = flow rate through the soil that reaches the lake, L^3/T

The theoretical range of exponents m, s, and q is from 0.0 to 1.0. In practice, m is usually 0.3-0.5, s is 0.4-0.7, and q = 0.5-0.8. Solving simultaneously, we obtain the solution for lake alkalinity through time.

$$(Alk) = (Alk)_o e^{-Qt/v} + \frac{k \frac{V_{soil}}{V} Mr}{\left(\frac{Q}{V} - k\right)} \left(e^{-kt} - e^{-Qt/V}\right)$$

$$- \frac{I}{Q} L_{acy} \left(1 - e^{-Qt/V}\right) \tag{25}$$

$$r = r_o e^{-kt} \tag{26}$$

Note that the alkalinity equation (25) consists of a first term describing the washout of initial conditions, a second term for alkalinity production in the watershed, and a third term related to the acid loading. After an increase in acid deposition, the solution to the equation (25) goes through a plateau at a pseudo-steady state, and then deteriorates to the input acidity (IL_{acy}/Q) as $t \rightarrow \infty$. In extremely sensitive systems, the time to steady state ($t_{95\%\ SS}$) can be as short as 100 years, but in most watersheds, $t_{95\%\ SS}$ is hundreds of years of more. The half-life of the soil neutralization capacity (ANC) is given by equation (27).

$$t_{1/2} = \frac{0.69}{k} \qquad (27)$$

Figure 9 gives the results for a hypothetical lake receiving acid precipitation at pH 4 for an extended period of time. It is an extremely sensitive system with shallow soil and low ANC. Using equations 22 and 23, the results indicate a relatively rapid response followed by a slow soil titration over hundreds of years. Hence even in very sensitive settings, there exist enough mineral bases to partially neutralize acid deposition for a very long time. However the additional input of acid deposition may be sufficient to depress soil pH.

It is possible to make the soil equations (23) and (26) more mechanistic by including two terms: a term for exchangeable bases and one for aluminosilicate weathering. The weathering of aluminosilicate minerals serves as a source term for the exchangeable base component of the soil ANC. This modifies the kinetics of soil titration somewhat by introducing a fast neutralization reaction with a relatively small buffer capacity (ion exchange) and a slower neutralization reaction with a relatively large buffer capacity

(mineral weathering). If the addition of fresh mineral bases to the soil (by solifluction or other processes) is small compared to acidic deposition, then the soil would lose all of its ANC over some period of time. In such a case, mineral weathering would be the rate determining step and equation (27) would give the half-life for the soil processes and the long-term resulting water chemistry. For the vast majority of cases within the time horizon of interest (decades to a few centuries), the amount of minerals in the soil and contributing bedrock can be considered to be in excess, and equation (20) gives the steady state alkalinity concentration in the lake after only a few water residence times.

6. SUMMARY

The pH and pε of the terrestrial and aquatic environment is determined by coupled reactions of oxidation-reduction and acid-base. If disturbances are created in elemental cycles of the environment (whereby oxidation of C, S, and N exceeds reduction reactions), a net production of H^+ ions is a necessary consequence. We have shown that aggrading biomass and humus and oxidation reactions (nitrification, sulfur oxidation) serve to add protons to aqueous systems, while chemical weathering, ion exchange, and reduction reactions (denitrification, H_2S production) serve to consume protons (add ANC to the water). Bar diagrams are a convenient means to examine changes in ANC or BNC in water and soils.

Atmospheric acid deposition creates an additional input of hydrogen and sulfate ions (H_2SO_4) to the terrestrial and aquatic ecosystem which is partly neutralized by increased weathering and cation export. It is balanced, in part, by aluminum dissolution and causes the negative effects in aquatic ecosystems on fish and possibly on forests.

The lakes which have been acidified by acid precipitation are those with extremely sensitive hydrologic settings and with watersheds lacking carbonate minerals. They tend to be small lakes. They respond relatively rapidly to changes in acid loading (on the order of a few hydraulic detention times). The soils of these watersheds have not been greatly acidified by acid precipitation nor has podzolization occurred due to anthropogenic acid deposition. However, this does not imply that more subtle changes in nutrient cycling or forest production could not have occurred. Soil solution pH could be reduced by the anthropogenic input of acids. We have proposed a quantitative framework with which to examine these questions.

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REFERENCES

[1] Sillén, L.G., "The physical chemistry of sea water " in: Oceanography. M. Sears ed., American Assoc. for the Advancement of Science, Washington, D.C. (1961).

[2] Broecker, W.S., "A kinetic model for the chemical composition of sea water", Quarternary Res., 1, 188 (1971).

[3] Stumm, W.; Morgan, J.J.; Schnoor, J.L., "Saurer Regen, eine Folge der Störung gydrogeochemischer Kreisläufe", Naturwissenschaften, 70, 216 /1983).

[4] Johnson N.M.; Driscoll, C.T.; Eaton, J.S.; Likens, G.E.and McDowell, W.H., "'Acid rain', dissolved aluminum and chemical weathering at the Hubbard Brook Experimental Forest, New Hampshire", Geochim. Cosmochim. Acta, 45, 1421 (1981).

[5] Schindler, P.W., "Surface complexes at oxide-water interfaces", in: Adsorption of Inorganics at Solid-Liquid Interfaces, M.A. Anderson and A.J. Rubin eds., Ann Arbor Science Publishers, Ann Arbor, MI (1981).

[6] Stumm, W.; Furrer, G. and Kunz, B., "The role of surface coordination in precipitation and dissolution of mineral phases", Croat. Chem. Acta, 56, 585 (1983).

[7] Kummert, R.; Stumm, W., "The surface complexation of organic acids on hydrous γAl_2O_3", J. Colloid Interface Sci., 75, 373 (1980).

[8] Fitzpatrick, E .A., Soils - Their Formation, Classification and Distribution, Longman, New York, N.Y., 1980.

[9] Correns, C.W., "The experimental chemical weathering of silicates", Clay Minerals Bulletin, 26, vol. 4, 249 (1961).

[10] Goldich, S.S., "A study in rock-weathering", Journal of Geology, 46, 17 (1938).

[11] Ulrich, B.; Mayer, R. and Khanna, P.K., "Chemical changes due to acid precipitation in a loess-derived soil in Central Europe", Soil Science, 130, 193 (1980).

[12] Ulrich, B., "Eine ökosystemare Hypothese über die Ursachen des Tannensterbens (Abies alba Mill.)", Forstwiss. Centralbl., 100, 228 (1981).

[13] Johnson, A.H.; Siccama, T.G., "Acid deposition and forest decline", Environ. Sci. Technol., 17, 294A (1983).

[14] Krug, E.C. and Frink, C.R., "Acid rain and acid soil: A new perspective", Science, 221, 520 (1983).

[15] Van Breeman, N.; Driscoll, C.T., Nature (1983),in press.

[16] Johnson, D.W.; Henderson, G.S.; Huff, D.D.; Lindberg, S.E.; Richter, D.D.; Shriner, D.S.; Todd, D.E. and Turner J., "Cycling of organic and inorganic sulphur in a chestnut oak forest", Oecologia, 54, 141 (1982).

[17] Galloway, J.N.; Norton, S.A.; Church, M.R., "Freshwater acidification from atmospheric deposition of sulfuric acid: A conceptual model", Environ. Sci. Technol.,17, 541A (1983).

and Likens, G.E.,)

[18] Driscoll, C.T.("Hydrogen ion budget of an aggrading forested ecosystem", Tellus, 34, 283 (1982).

[19] Emerson, S. and Bender, M., "Carbon fluxes at the sediment-water interface of the deep-sea: Calcium carbonate preservation", J. Marine Research, 39, no. 1, 139 (1981).

[20] Kuivila, K.M., and Murray, J.W., "Organic matter diagenesis in freshwater sediments: The alkalinity and total CO_2 balance in the sediments of Lake Washington", Limnol. Oceanogr., in press.

[21] Schnoor, J.L.; Sigg, L.; Stumm, W. and Zobrist, J., "Acid precipitation and its influence on Swiss Lakes", EAWAG News,14/15, 6 (1983).

[22] Schnoor, J.L.; Palmer, W.D., Jr.; Glass, G.E. In: Modeling of Total Acid Precipitation Impacts, Schnoor ed., Butterworth Publishers: Woburn, MA, 1984.

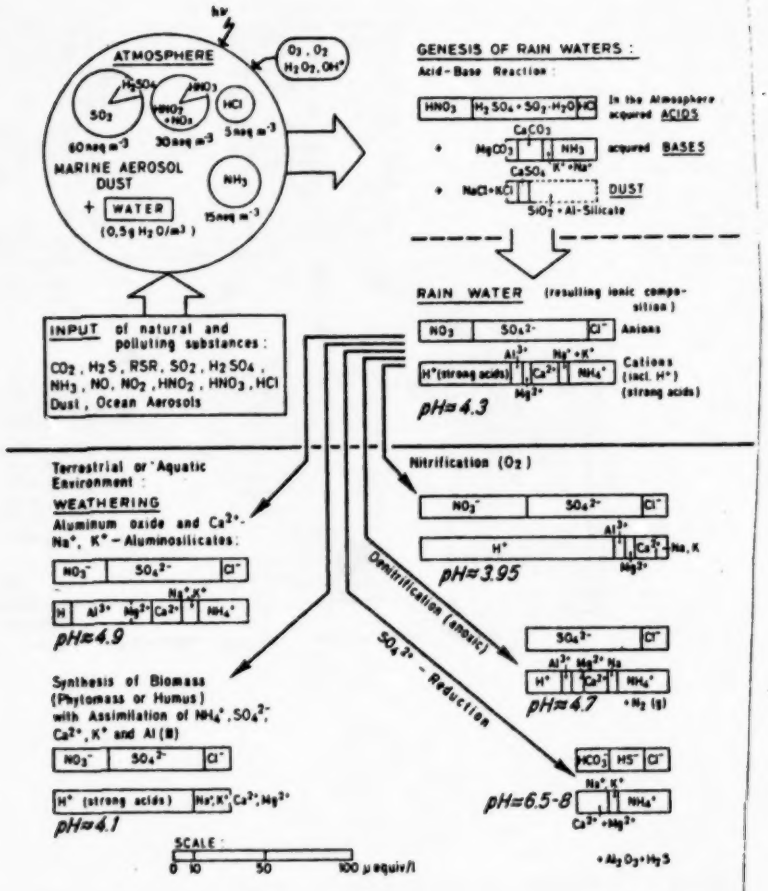


Figure 1

Genesis of acid rain (from Stumm, Morgan Schnoor [3])
From the oxidation of S and N during the combustion of fossil fuels, there is a build-up in the atmosphere (in the gas phase, aerosol particles, rain drops, snow flakes and fog) of CO_2 and the oxides of S and N, which leads to acid-base interaction. The importance of absorption of gases into the various phases of gas, aerosol, and atmospheric water depends on a number of factors. (In this figure, we assume a yield of 50% for SO_4^{2-} and NO_3^-, of 80% for NH_3 and of 100% for HCl.) The genesis of acid rain is shown on the upper right as an acid-base titration. Various interactions with the terrestrial and aquatic environment (see Table 1) are shown in the lower part of the figure.

The data given are representative of the situation encountered in Zurich, Switzerland

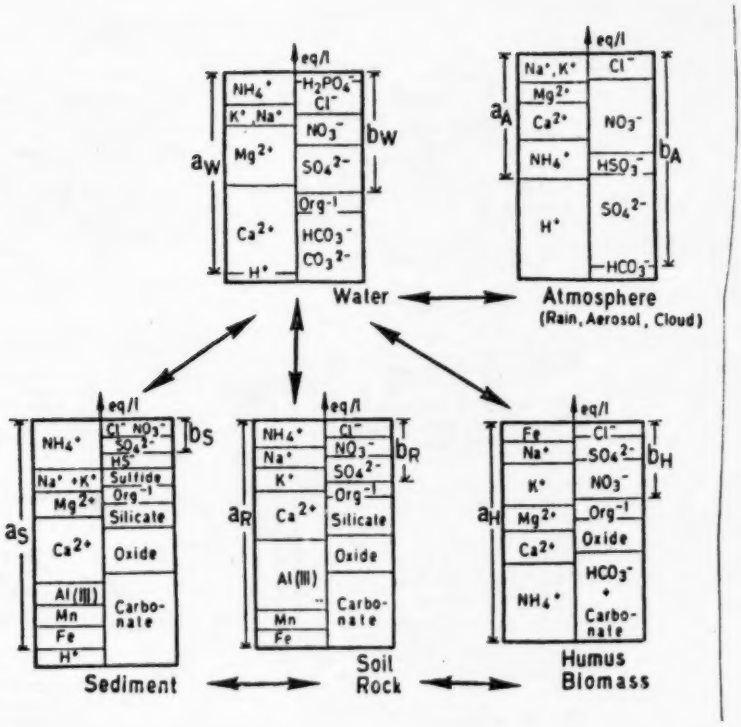


Fig. 2 Transfer of Alkalinity or Acidity Between Atmosphere, Water, Soil (Rocks), Sediments and Biota (Humus)

In a (hypothetically closed) large system of the environment (atmosphere, hydrosphere, lithosphere) a proton and electron balance is maintained. Temporal and spatial inhomogeneities between (and within) the individual reservoirs may cause significant shifts in electron and proton balances so that subsystems contain differences in alkalinity and acidity. Any transfer in ions from one substance to another - however caused, by transport, chemical reaction or redox processes - causes a corresponding transfer of [Alk] (or H-Acy).

For each subsystem, the acid-neutralizing capacity [Alk] or the base-neutralizing capacity [H-Acy] can be defined in terms of the difference between the equivalent sum of base cations and that of conservative anions:

$$[Alk]_{Wat.} = a_W - b_W = -[H\text{-}Acy]_{Wat.}$$

$$[Alk]_{\substack{Soil\\Rock}} = a_R - b_R = -[H\text{-}Acy]_{\substack{Soil\\Rock}}$$

$$[Alk]_{Sed.} = a_S - b_S = -[H\text{-}Acy]_{Sed.}$$

$$[Alk]_{\substack{Humus\\Biomass}} = a_H - b_H = -[H\text{-}Acy]_{\substack{Humus\\Biomass}}$$

$$[Alk]_{Atm} = a_A - b_A = -[H\text{-}Acy]_{Atm.}$$

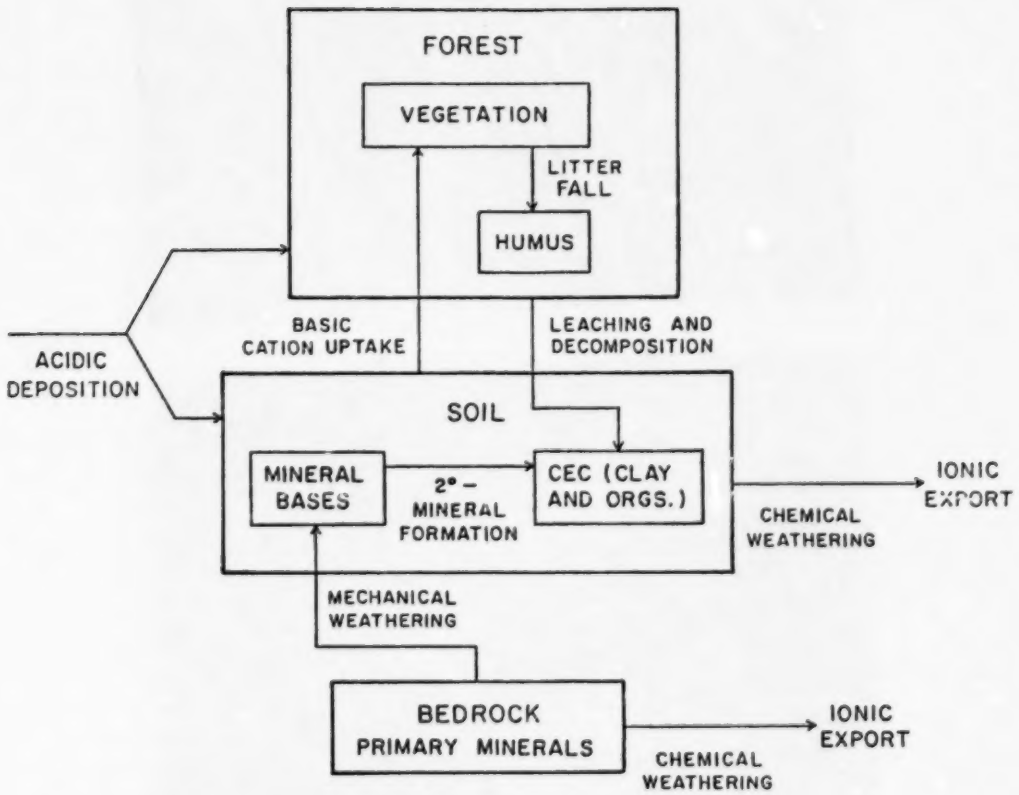


Figure 3 Process Affecting the Acid-Neutralizing Capacity of Soils (including the exchangeable bases, CEC, and mineral bases).

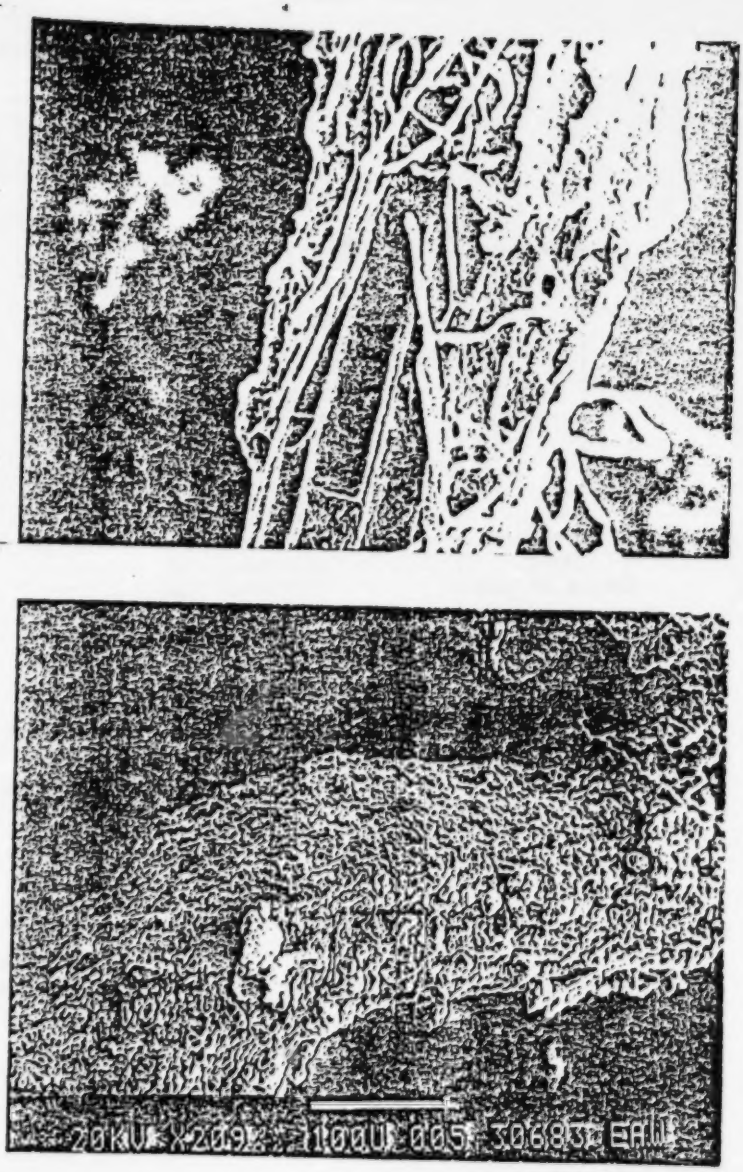


Figure 4. Scanning Electron Microphotographs of Spruce Roots.

Fine roots from Norway spruce trees.
(Picea abies Karst.) in Harz Mountains, Lange Bramke watershed, West Germany. Soil pH = 3.8.
(Top: healthy root. Energy Dispersive System (EDS) spectra showed qualitatively that aluminum is the predominate cation on the surface of the root and mycorrhizal fungi.)
(Bottom: root from dying tree. fine, healthy roots were not observed. Surface of this root was scaly, and EDS spectra indicated the presence of Si, Al, Fe, K cations, in rank order, on the surface of the root.)

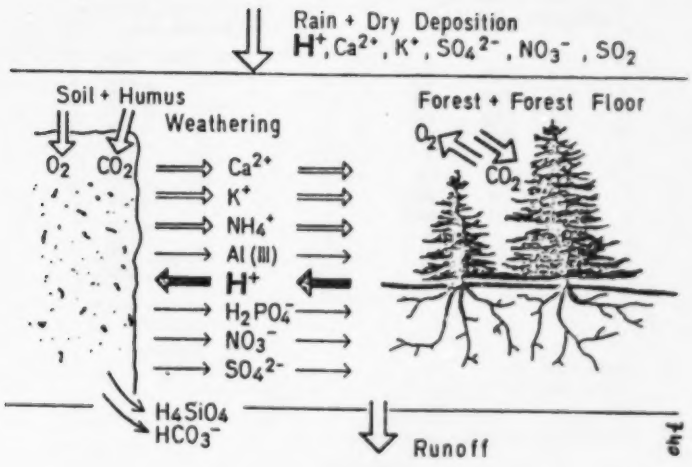
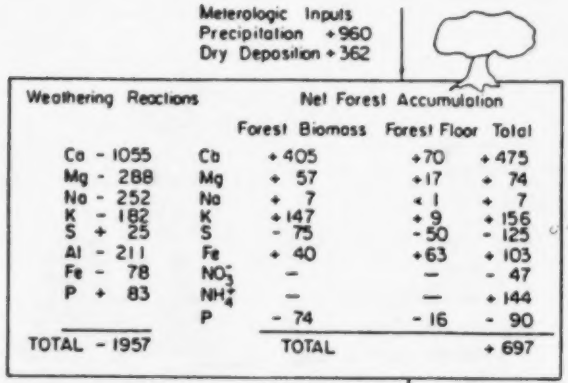


Figure 5 Competition between H^+ release by growing trees (aggrading forest) and H^+ consumption by soil weathering

HUBBARD BROOK HYDROGEN ION BUDGET (in eq H^+ ha^{-1} yr^{-1})



SUMMARY

Hydrogen Ion Sources	+ 2541
Hydrogen Ion Sinks	- 2428
Budget Discrepancy	+ 113

Figure 6 Budget of H^+ Sources and H^+ Sinks in Hubbard Brook Ecosystem

from Driscol and Likens [18]

H^+ ion released or consumed in equivalents $hectare^{-1}$ $year^{-1}$ as a consequence of ion uptake by the aggrading forest biomass (+ forest floor) and ion release by weathering reactions, respectively.
Because of atmospheric deposition of acid, H^+ sources nearly balance H^+ sinks

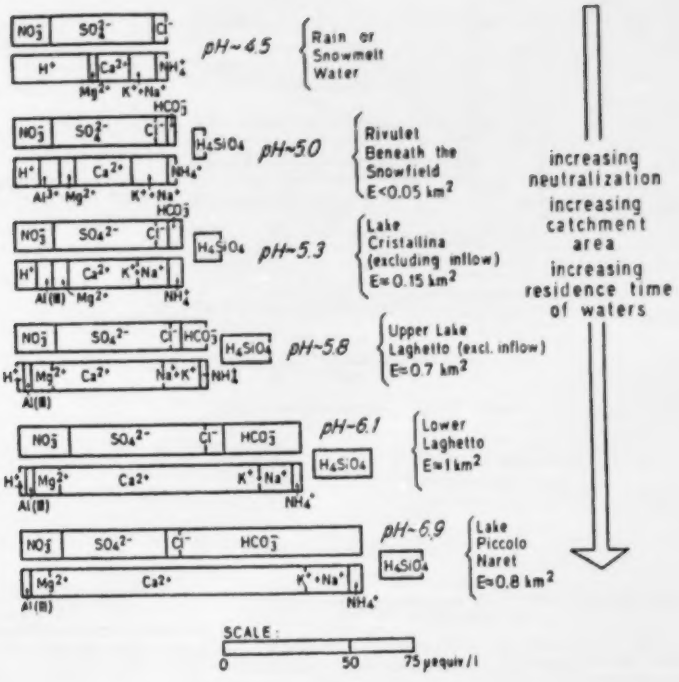


Figure 7 from Schnoor, Sigg, Stumm and Zobrist [21]

Chemical composition of several waters in a drainage pattern in the area of the upper Maggia valley (in the vicinity of the Naret dam, at 2100–2500 m)

The extent of acid neutralization of rain or snowmelt water (chemical weathering) increases with the relative catchment area, E, and thus the residence time of the waters.

This neutralization is accompanied by increases in pH, silicic acid concentration (H_4SiO_4), and by the liberation of cations from dissolution. Because of hydrologic changes from snowmelt, there are seasonal variations. This figure gives the condition from measurement at the of end July, 1982.

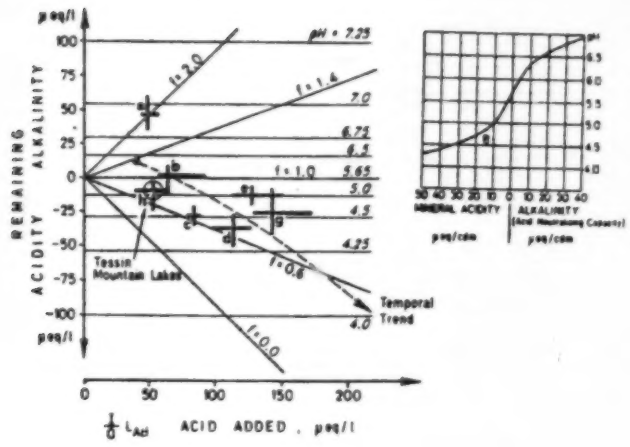


Figure 8

Alkalinity of natural waters as a function of Acid Loading (modified from [22])

The acid deposition in the drainage area of lakes is neutralized by chemical weathering (the reaction with bases contained in rocks and minerals). f is the equivalents of acid neutralized by weathering (f = 0 signifies no neutralization; f = 1 corresponds to a perfect buffer; f > 1 signifies an alkalization of the water, for example the dissolution of $CaCO_3$ by CO_2).

The difference between the acidity added and the resulting alkalinity corresponds to the degre of neutralization. Each lake would follow a titration curve (similar to the one on the upper right) with progressive acid loadings. The dashed line represents the temporal trend or reaction pathway as more acid is added to the system. It corresponds to the titration curve.

a and b are lakes in Minnesota and Wisconsin (USA); c represents the Birkenes stream and two other lakes in southern Norway; d signifies 5 lakes in southwest Sweden; e are waters in New York and New Hampshire (USA); g representents 6 lakes in the La Cloche Mountains of southern Ontario, Canada; h indicates the Swiss Lakes in the upper Maggia valley of Tessin,

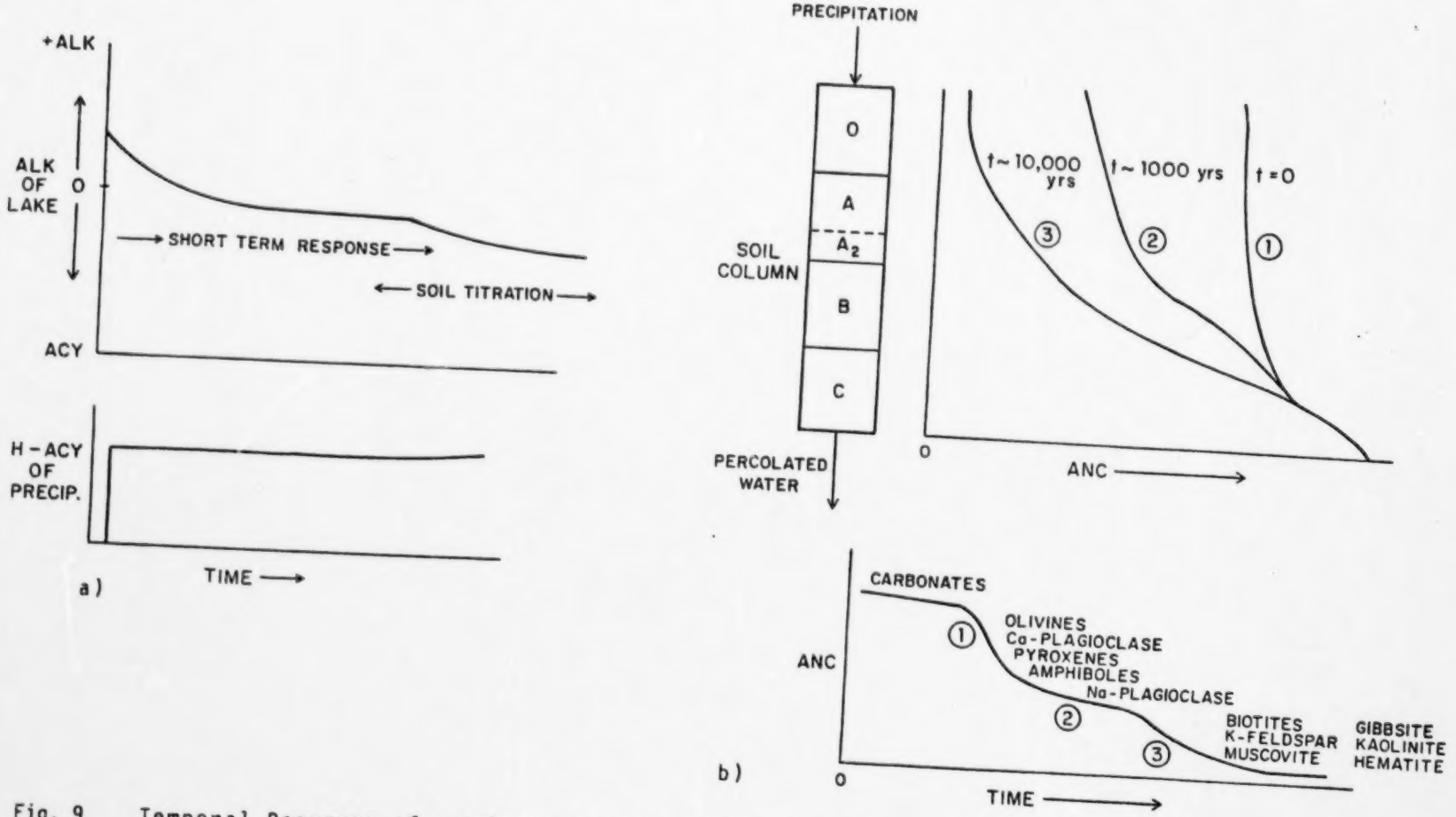


Fig. 9 Temporal Response of a Lake to Acid Precipitation (pH = 4)

a) Acidification of Lake over Long Time. (Short term response is over a period of a few years. Longterm soil titration takes from a few decades to centuries).

b) Corresponding Soil Titration